

Stability, Electronic Structure and Vibrational Modes of Ti_8C_{12} Dimer

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We present our density functional results of the geometry, electronic structure and dissociation energy of Ti_8C_{12} dimer. We show that as opposed to the currently held view that Ti_8C_{12} are highly stable monodispersed clusters, the neutral Ti_8C_{12} clusters form covalent bonds and form stable dimers. We determine that the Ti atoms bond weakly (0.9 eV/bond) to organic ligands such as ammonia. Alternatively the Met-Car dimer has a cohesive energy of 4.84 eV or approximately 1.2 eV per bond. While Met-Car dimers are stable, formation of these dimers may be quenched in an environment that contains a significant population of organic ligands. The ionization and dissociation energies of the dimer are of same order which prevents the observation of the dimer in the ion mass spectroscopy. The analysis of the vibrational frequencies show the lowest-energy structure to be dynamically stable. We also present infrared absorption and Raman scattering spectra of the Ti_8C_{12} dimer.

The Ti_8C_{12} clusters consisting of eight metal and twelve carbon atoms were found to be highly stable.^{1,2} Such clusters of other sizes were found to be less abundant as seen from the mass-abundance spectrum reported by Castleman and his co-workers.¹ Apart from Ti atoms, similar clusters with eight metal atoms were found to form with other transition metals such as V, Zr, Hf, Nb, Mo, Fe, Cr^{1,2,3,4} etc. These metallocarbohedrene clusters are generally referred to as Met-Cars. A detailed account of the various Met-Cars can be found in Ref..⁵

The ground state structure of Met-Cars has generated a lot of debate. The early studies have assigned a structure with T_h symmetry which later on was shown to be Jahn-Teller unstable.^{6,7} Dance⁷ has shown the existence of a barrierless transition path from T_h leading to a T_d structure. Another calculation by Chen *et al.*⁸ have proposed a D_{2d} structure for the Ti_8C_{12} . Recently, Gueorguiev and Pacheco⁹ have shown that Jahn-Teller distorted T_d structure is lowest in energy among the T_h , T_d , and D_{2d} structures. A recent calculation by the present authors found the Met-Cars to possess a C_{3v} structure which is lower in energy than either the T_d or the D_{2d} structures.¹⁰

An important aspect of these clusters is their paradoxical nature - while they are highly stable in vacuum they are found to be very air sensitive. The ionization potential and electron affinity of the Met-Cars suggest that these clusters have moderate reactivity.^{10,13,14,15} Another such issue which has not yet been studied is the formation of larger clusters in which the individual Met-Cars are the building blocks. It may be mentioned here that Met-Cars of various sizes, e.g. $\text{T}_{13}\text{C}_{22}$ exist but their structures show them to be different from Ti_8C_{12} .^{11,12} They can not be considered as made up from Met-Car units. In this article, we examine the possibility of two Met-Cars coalescing to form a stable dimer. We show that a dimer connected through four-membered rings of Ti and C atoms form a stable structure in which both the individual Met-Cars retain their identity. This may form a basis for future studies on Met-Car based molecular

solids. We also present the calculated infrared absorption and the Raman spectra of the Ti_8C_{12} dimer. We believe this may help in identifying the Met-Car dimers in experimental IR and Raman spectra.

The theoretical calculations were carried out within the density functional theory²¹ using a linear combination of atomic-orbitals (LCAO) approach. The calculations were performed using the NRLMOL²² program which employs a Gaussian basis set. The molecular orbitals were expanded as linear combinations of Gaussian functions centered at the atomic sites. The exponents for the single Gaussians have been fully optimized for DFT calculations.²³ The calculations were carried out at the all-electron level with the generalized gradient approximation to the exchange-correlation functional.²⁴ A variational mesh is used to reduce the computation as well as storage of data and still maintain the high accuracy of the calculations.²⁵ The code is massively parallelized²⁶ which allows one to perform calculations on a cluster of PCs. The geometry optimization was carried out using the conjugate-gradient technique. The self-consistent calculations for each geometry was carried out till the energy difference fell below 1.0×10^{-6} a.u., so as to obtain accurate forces. The force minimization was carried out to a tolerance limit of 0.001 a.u on each atom.

The calculation of infrared absorption and Raman scattering spectra were performed according to the method described in Ref..²⁷ The dynamical matrix is generated by moving the atoms by $\sim \pm 0.08$ a.u. from their equilibrium positions. The Raman and infrared intensities are obtained by applying an electric field of strength 0.005 a.u. and calculating the first and second derivatives of the dipole moment and polarizability with respect to the applied electric field.

Our earlier calculations have shown that the lowest energy structure of the neutral Ti_8C_{12} possesses C_{3v} symmetry¹⁰ while the D_{2d} and the T_d structures lie slightly higher in energy. We have also determined that both the C_{3v} and D_{2d} structures are vibrationally stable. To determine the lowest-energy structure of the

Ti₈C₁₂ dimer, we started out by considering several different dimers composed of two C_{3v} structures. A schematic diagram of the optimized structures of the various dimers is shown in Fig. 1. The figure shows the metal cages with the carbon dimers lying on the surfaces of each Met-Car. The bonds between the Met-Cars are also pointed out. The first structure that we studied retains the C_{3v} structure and tests whether a Ti-Ti “bond” may form. This corresponds to structure (a) in Fig. 1. Since the two Met-Cars are related by inversion, the overall symmetry of this dimer is D_{3d}. This structure may exist in either the staggered or eclipsed form (Fig. 1(b)). The second structure that we considered was determined by allowing two C-C dimers to form 4-membered rings. This corresponds to structure (c) in Fig. 1. The underlying C_{3v} symmetry of this structure is broken and the final symmetry consists of the 8-membered group generated by all reflections. Another structure, labeled (d) in the figure, may be generated by allowing 4-membered Ti-C-Ti-C rings to connect the two Met-Cars. This structure is bound relative to two C_{3v} Met-Cars by 2.9 eV. The four-membered ring is composed of intra- and inter- molecular Ti-C bonds of 1.96 Å and 2.15 Å respectively. The symmetry group is generated by inversion and (xyz) ⇒ (zyx). Examination of this structure shows that an intermolecular Ti₄C₄ cubane unit may be formed by bending the respective Met-Cars out of the planar ring and toward one another. This leads to structure (e) in Fig. 1. The resulting TiC is composed of bondlengths that average 2.18 Å. However, the cubane connector is distorted with both long (2.32 Å) and short (2.04 Å) bonds forming the intramolecular faces and medium (2.18 Å) bonds forming the intermolecular bonds. This dimer structure is comprised of 4 Ti-C bonds between the neighboring balls. It is bound by 4.84 eV or approximately 1.21 eV per Ti-C bond. This structure has only one symmetry operation (xyz) ⇒ (-x,y,-z). The binding energy per Ti-C bond is similar to the energy we found for the Ti-N bonds in our titration calculations discussed later. Within the symmetry constraints discussed above, the geometry of these structures were modified until the forces on atoms were less than 0.001 a.u. We wish to point out that while carrying out the optimization, the symmetry of the individual Met-Cars was not enforced, rather the Met-Cars were allowed to relax while forming a dimer. This will allow the individual MetCars to relax into symmetry allowed structures other than C_{3v} while forming the dimer.

We find the structure labelled as (e) to possess the lowest energy among all the structures considered. In Table I, we present the relative energies of the dimers with respect to the energy of (e). The dissociation energies required for the dimers to dissociate into the constituting Met-Cars are also presented. The dissociation energy of the structure (e) is highest showing it to be the most structurally stable form. In Table I we also present the HOMO-LUMO gaps of all the structures. The HOMO-LUMO gap of the (b) structure is highest followed by that of the structure (e) while in structures (c) and (d) the gap

is small which will show more metallic behavior and also higher chemical reactivity. To assess the chemical reactivity of the lowest-energy dimer, we also calculated the vertical ionization potential and electron affinity (VEA). In this calculation, the charged clusters were not allowed to relax. The VIP of the structure (e) is 4.4 eV while the VEA is 1.3 eV. The VIP is of the same order as that of a single Met-Car (4.47 eV) while the VEA of the dimer is higher than that of Ti₈C₁₂ (1.05 eV).¹⁰ The reactivity of the dimer is therefore higher than that of single Ti₈C₁₂.

To investigate the retention of individual symmetry of the Met-Cars while forming a dimer, we studied the energy surface of the dimer as a function of Ti₈C₁₂ - Ti₈C₁₂ distance. In this case, the symmetry of the Met-Cars were maintained while the distance between them was varied. The energy vs. dimer separation curve is shown in Fig. 2. The minimum in the curve indicates the equilibrium separation when the individual Met-Car’s geometries do not relax. This minimum energy point is close to the structure (d) in Fig. 1. The difference between the equilibrium point in Fig. 2 and the structure (d) arises from the fact that in structure (d) the symmetry of the individual Met-Cars were not retained and therefore the energy of structure (d) is lower. The small energy difference (0.1 eV) suggests that the symmetry distortion is small in the structure (d).

Another relevant question is how stable a molecular solid made from Ti₈C₁₂ would be. Our calculations show that an isolated Met-Car dimer would form chemical bonds and lead to a binding energy per Met-Car of approximately 2.42 eV. For chemically bound systems, this is on the weak side which suggests that a condensed phase of Met-Cars may behave differently. For example, when the Met-Car center-to-center distance is increased by 2.0 au, the intermolecular chemical bonds are completely broken and the isolated structure of the Met-Cars is retained. However we find that this structure is still bound by 0.285 eV/Metcar which would suggest an FCC lattice of Met-Cars would be bound by roughly $12 \times 0.285 / 2 = 1.8$ eV per Met-Car. Such a lattice might be further stabilized by some metallic bonding due to the unclosed electronic shell. As such the weak covalent bonds formed for a Met-Car dimer may not be strong enough to survive in the condensed phase and a lattice of isolated Met-Cars is at least competitive. The binding energy of the dimers for the same particle-particle separation but averaged over different orientation is about 0.06 eV/Met-Car which by the above analysis shows a binding energy in the crystalline environment to be about 0.36 eV. This is much more weak than predicted by the earlier considerations. Additional calculations on the bulk phase would be useful for clarifying this point.

While our results show that the Met-Car dimer is stable with respect to separated Met-Cars, observation of this dimer will almost certainly require an environment devoid of ligands. The reactivities of Met-Cars have not yet been fully explored. Some investigations on the reaction of Met-Cars with molecular oxygen have been

reported.^{16,17,18} An ab initio calculation by Ge *et al.*¹⁹ on $\text{Ti}_8\text{C}_{12}(\text{H}_2\text{O})_8$ and $\text{Ti}_8\text{C}_{12}(\text{C}_2\text{H}_4)_4$ have shown the stability of the Ti_8C_{12} to increase upon reaction with water while it decreases in reaction with C_2H_4 . Another calculation by Poblet *et al.*²⁰ have shown an exothermic reaction for addition of Cl, NH_3 , CO, C_6H_6 . They also showed that addition of eight ammonia or Cl is easy while adducts with eight CO or benzene is difficult. To check whether the energy ordering of Met-Cars with different symmetry is influenced by absorption of radicals, we have carried out optimizations of the geometries of the Met-Car in T_d and T_h and eight ammonia molecules bonding with the Ti atoms. The energy of the ammonia covered T_d structure is significantly lower than that of the T_h structure. However, the vertical ionization potential (VIP) of these two structures do not follow the same trend. The VIP of the ammonia covered T_h structure is 2.76 eV while that of the T_d structure is 2.41 eV. The binding energy of the lowest structure with respect to the dissociation into eight ammonia molecules and the Ti_8C_{12} is 7.43 eV which suggests an average of 0.93 eV per bond. The structure of the Met-Cars after absorption of eight ammonia retains the symmetry thereby implying that the structure does not change upon reaction. Our calculated Ti-NH_3 binding energy of 0.9 eV is similar to other calculated Ti-ligand binding energies. For example, Ref.¹⁹ and²⁰ find binding energies for Cl, NH_3 , CO, and to H_2O be in the range of 0.5 eV (CO) to 2.3 eV (H_2O). In an ammonia rich environment the system could either form a dimer with at most 12 adsorbed NH_3 ligands or two monomers with a total of 16 adsorbed NH_3 ligands. Steric effects would probably prevent a total of 12 adsorbed NH_3 ligands on the dimer and would also weaken the Ti-NH_3 bonds. The former structure would have energy of at most 15.6 eV while the latter structures would have an energy of 14.4 eV. Steric effects would probably lower the ligandated dimer below that of two ligandated monomers and kinetic considerations would also favor growth of the separated ligandated monomers. These considerations may also explain why the Met-Cars seem to be stable in soot.

To facilitate an understanding of the possible molecular processes which could hinder the observation of the dimer formation, we have compared the dimer total energy with that of $\text{Ti}_{13}\text{C}_{22}$ and Ti_3C_2 . The $\text{Ti}_{13}\text{C}_{22}$ is earlier reported to be stable^{11,15} which has a cubic structure. We found that such a process would cost an energy of 12.3 eV for the lowest-energy structure predicted in Ref.11 which ruled out any possibility of the dimer fragmentation into these products. On the other hand, the ionization energy of the dimer (~ 4.4 eV) is of the same order as the energy required for dissociation into monomers (4.84 eV). Since the mass spectrography measurements are carried out on ionized clusters, the ionization process is likely to induce dissociation. A detailed investigation of the dimer cation is beyond the scope of the present work.

We have also calculated the vibrational modes of the

lowest-energy structure of the dimer. The calculations show the dimer to possess no imaginary frequencies thereby indicating that the structure (e) indeed refers to an equilibrium structure. One noticeable feature of the vibrational modes is that this structure exhibits a few low frequency modes which are absent in the individual Met-Car vibrational modes.¹⁰

The IR absorption spectrum of the dimer is shown in Fig. 3 (upper panel). The spectrum has been broadened with a Gaussian of full width half maximum of 40 cm^{-1} . In the low frequency region, peaks occur at 186, 241, 260, 272, 280, 292, and 330 cm^{-1} which corresponds to Ti-C stretching and also twisting modes. In the single Met-Car, IR active peaks at the low frequency range are observed at 183, 204, 244, 266, 271, 373, 467, 517, and 559 cm^{-1} which are due to Ti-C stretching mode.^{9,10,28} In the slightly higher frequency region, the dimer IR spectrum closely resembles that of the Met-Car IR spectrum with a relatively large peak around 460 cm^{-1} and 550 cm^{-1} . These are actually composed of peaks at 460, 464, 472, 480, 527, 541, 551 cm^{-1} . These correspond to the C-C twisting modes and also translation of a carbon dimer on each Met-Car which leads to stretching of the Ti-C bonds. In the high frequency region, the spectrum shows a pronounced broad peak slightly beyond 1400 cm^{-1} . In fact this broad peak consists of three narrowly spaced peaks at 1411, 1417, and 1446 and another large peak at 1493 cm^{-1} . These correspond to C-C stretch modes in which all carbon dimers except the ones forming the four membered ring, take part. Other two smaller peaks appearing at 1349 and 1354 cm^{-1} are due to the C-C stretch mode involving only the carbon dimers forming the Ti_8C_{12} - Ti_8C_{12} bonds. It may be mentioned here that our calculation of the Met-Car IR spectrum shows a pronounced peak near 1400 cm^{-1} which also arises due to the C-C stretch mode. In the dimer, this peak appears to be shifted to the high frequency region.

Figure 3(lower panel) shows the Raman scattering spectrum of the Ti_8C_{12} dimer. In this case, a broad peak occurs in the low frequency region below 700 cm^{-1} . As mentioned earlier, there are a few low frequency vibrational modes which are Raman active. The first peak is comprised of two narrow peaks occurring at 44 and 84 cm^{-1} . These correspond to Ti_8C_{12} - Ti_8C_{12} bond stretch modes. The highest peak at about 200 cm^{-1} consists of narrow peaks at 185, 203, and 207 cm^{-1} corresponding to twisting and squeezing of the Ti-C and Ti-Ti inter-Met-Car bonds. The shoulder seen about 260 cm^{-1} is also due to Ti-C bonds forming the Ti_4C_4 cubane joining the two Met-Cars. The other noticeable peaks in the broad spectrum around 337 cm^{-1} occur due to Ti-C stretching where the Ti is part of the cubane, around 480 which is due to Ti-C squeezing mode. The smaller peaks around 591 cm^{-1} and 687 cm^{-1} are due to, respectively, the C-C stretching mode where one atom of the C-C dimer is a member of the cubane and a rocking motion of some of the carbon dimers which do not form part of the cubane. The high frequency spectrum

shows two prominent peaks. One peak consists of narrowly spaced peaks at 1367 and 1375 cm^{-1} and the other of peaks at 1417, 1448 and 1500 cm^{-1} . All of these correspond to C-C stretching modes of which the 1367 and 1375 cm^{-1} correspond to the stretching and squeezing of the C-C dimers involved in the formation of the cubane. The above results show that the vibrations involving Ti-C bonds occur at lower frequency and are Raman active whereas the C-C stretch modes occur at high frequency and are IR active. Similar features are seen in case of the IR and Raman spectrum of the single Met-Car¹⁰ although the spectrum is slightly shifted in frequency. The low frequency modes ($< 100 \text{ cm}^{-1}$) seen in the dimer are not visible in the single Met-Car spectra¹⁰ which as mentioned above arise from the vibrations involving the Ti and C atoms forming the Met-Car-Met-Car bonds.

In conclusion, we have carried out first principle density functional based study of the structure and stability

of Ti_8C_{12} dimer. Our calculations have shown the dimer to be stable by 4.84 eV. An analysis of the vibrational frequencies show the structure to be a local minimum. The IR and Raman spectrum of the dimer are presented and analyzed. The IR active modes are found in the high frequency region while the Raman active ones are located in the low-frequency region of the spectra. The symmetry of the individual Ti_8C_{12} 's are somewhat modified in the formation of the dimer. Our calculation predicts that a Met-Car solid will be weakly bound. From the ionization potential and the dissociation energy of the dimer, we predict that during the ionization process in the mass spectrography, the dimer is likely to dissociate into two Met-Car monomers which accounts for the lack of experimental observation of the dimer.

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TABLE I: The energies of the Met-Car dimers relative to the lowest energy structure, the dissociation energies (E_d) and the HOMO-LUMO gap (Δ) of the $[\text{Ti}_8\text{C}_{12}]_2$ clusters. The labels of the clusters are consistent with the Fig. 1.

	Relative energy eV	Dissociation energy eV	HOMO-LUMO gap eV
(a)	4.17	0.67	0.08
(b)	4.17	0.67	0.22
(c)	3.66	1.18	0.03
(d)	1.98	2.86	0.04
(e)	0.00	4.84	0.13

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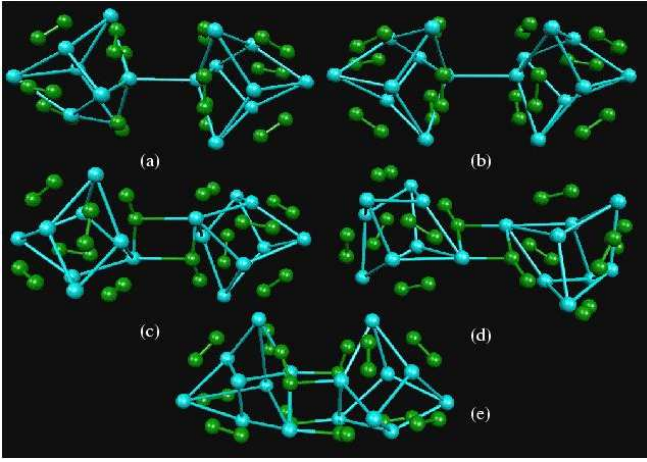


FIG. 1: The various dimer configurations considered in the present work. The metal cage structure with the carbon dimer on the surface of each Met-Car is highlighted. Also, the bonds between the Met-Cars are shown.

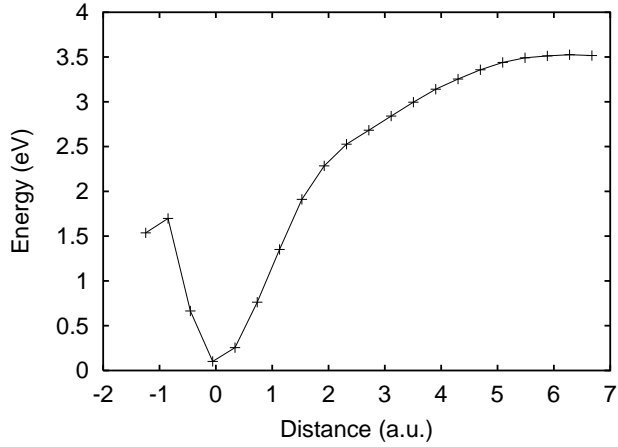


FIG. 2: The potential well formed when two Met-Cars are brought closer without relaxation. The relative energies and the distances are given with respect to the dimer (d) in Fig. 1.

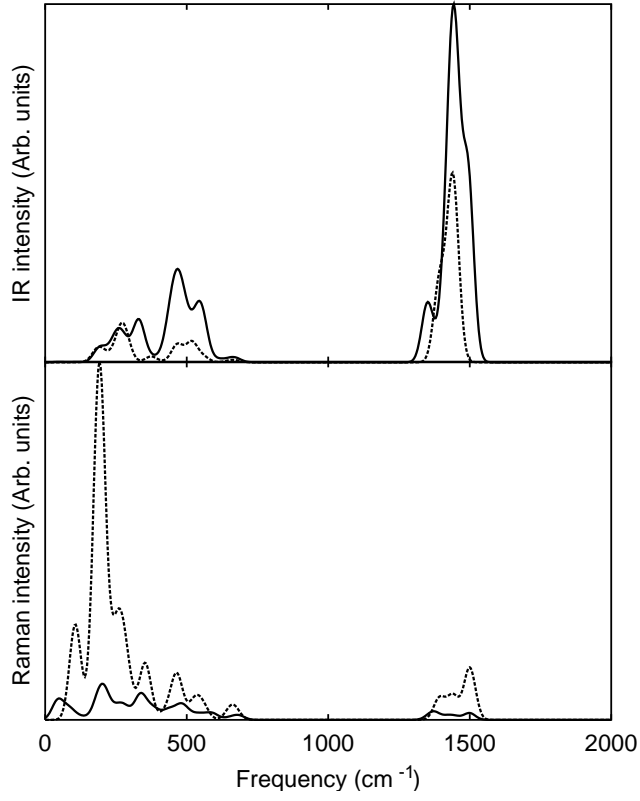


FIG. 3: The infrared absorption and Raman scattering spectra of the lowest-energy structure of Ti_8C_{12} dimer (solid lines) and the Ti_8C_{12} monomer (dashed lines) with C_{3v} symmetry. The intensities are broadened with a Gaussian of FWHM of 40 cm^{-1} .